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A study was carried out on the methylation of 5-(3-phenylureido)- and 5-amino-1,-2,3-thiadiazole-4-carbothioamides. A new rearrangement was observed for 5-amino-1,2,3-thiadiazole-4-S-methylcarbothioimidates to give 5-methylthio-1,2,3-tri-azole-4-carbothioamides.

Thioiminoesters of 1,2,3-thiadiazole-4-carboxylic acid have not been described in the literature. However, these compounds hold interest due to the chemical activity of the thioimidate group as starting reagents for the preparation of new 1,2,3-thiadiazole derivatives with potential as pesticides [1].

In order to obtain such compounds, we studied the methylation of 5-(3-phenylureido)-(I) and 5-amino-1,2,3-thiadiazole-4-N-R-carbothioamides (IIa) and (IIb) by methyl iodide.

Despite the presence of several reaction sites in (I), its treatment by methyl iodide in the presence of sodium ethoxide gives pure 5-(3-phenylureido)-1,2,3-thiadiazole-4-S-methylthioimidate (III) in high yield. The structure of (III) was supported by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.



Thioamides (IIa) and (IIb) have higher reactivity than (I) and react with methyl iodide both in the presence and absence of bases. However, thioimidates (IVa) and (IVb) are unstable and rearrange to 5-methylthio-1,2,3-triazole-4-carbothioamides (Va) and (Vb). The structures of (Va) and (Vb) were indicated by IR, UV, PMR, and <sup>13</sup>C NMR spectroscopy and mass spectrometry as well as synthesis from 5-mercapto-1,2,3-triazole-4-carbothioamides (VIa) and (VIb) and methyl iodide.



The conversion of thiadiazoles (IVa) and (IVb) to triazoles (Va) and (Vb) apparently proceeds through the formation of intermediate diazo compounds (VIIa) and (VIIb) and is a new rearrangement of 1,2,3-thiadiazoles to 1,2,3-triazoles involving the nitrogen atom of the thioimidate group.

We should note that such a recyclization is the first example of the generation of aliphatic diazo compounds containing C=S and C=N bonds in the  $\alpha$ -position.

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## EXPERIMENTAL

The reactions and the purity of the compounds were monitored by thin-layer chromatography on Silufol UV-254 plates. The IR spectra were taken on a Specord IR-75 spectrometer in KBr pellets. The UV spectra were taken on a Beckman M-26 spectrophotometer in ethanol. The PMR spectra were obtained on a Bruker WR-80 spectrometer at 80.23 MHz in DMSO-d<sub>6</sub> with TMS as the internal standard. The <sup>13</sup>C NMR spectra were taken on a Bruker WR-80 spectrometer at 20.13 MHz in DMSO-d<sub>6</sub> with TMS as the internal standard. The mass spectra were taken on a Varian MAT-311A mass spectrometer at 70 eV.

5-(3-Phenylureido)-1,2,3-thiadiazole-4-carbothioamide (I). A sample of 0.12 ml (0.97 mmole) Et<sub>3</sub>N and 1.05 ml (9.7 mmoles) phenyl isocyanate were added with stirring to a solution of 1.55 g (9.7 mmoles) 5-amino-1,2,3-thiadiazole-4-carbothioamide (IIa) [2] in 5 ml DMF. After 5 min, the residue was filtered off and crystallized from ethanol. The yield of (I) was 2.1 g (78%), mp 208-209°C (dec.). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3280, 3220, 3130 (NH), 1700 (C=O). UV spectrum ( $\lambda_{max}$  (log  $\varepsilon$ ), nm): 205 (3.35), 225 (3.22), 284 (3.45). PMR spectrum ( $\delta$ , ppm): 7.1-7.7 m (Ph), 10.0 s (NH<sub>2</sub>), 10.7 s (NH), 12.4 s (NH). Found: C, 43.4; H, 3.4; N, 24.8; S, 23.0%. Calculated for C<sub>10</sub>H<sub>9</sub>N<sub>5</sub>OS<sub>2</sub>: C, 43.0; H, 3.2; N, 25.1; S, 22.9%.

5-Methylthio-1,2,3-triazole-4-carbothioamide (Va). A sample of 1 g (6.0 mmoles) thiadiazole (IIa) (method A) or triazole (VIa) [2] (method B) was added to a solution of sodium ethoxide prepared by dissolving 0.14 g (6.0 mmoles) sodium in 10 ml abs. ethanol. Then, 0.8 ml methyl (12.0 mmoles) methyl iodide was added dropwise with stirring at 0-5°C. After 5 min, the precipitate was filtered off and crystallized from ethanol. The yield of (Va) was 0.55 g (60%) (method A) and 0.75 g (83%) (method B).

Method B. A sample of 0.8 ml (12.0 mmoles) methyl iodide was added with stirring to a suspension of 0.14 g (6.0 mmoles) thiadiazole (IIa) in abs. ethanol. The reaction mixture was maintained for one month at about 20°C or heated at reflux for 6 h. The precipitate was filtered off and recrystallized from ethanol. The product yield was 0.55-0.73 g (60-81%). The physicochemical indices of the samples obtained by all the methods fully coincide, mp 160°C. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3385, 3290, 3180 (NH), 3050, 2910 (CH). UV spectrum ( $\lambda_{max}$  (log  $\varepsilon$ ), nm): 214 (3.07), 249 (2.76), 293 (2.97). PMR spectrum ( $\delta$ , ppm): 2.5 s (SMe), 9.2 s, 9.4 s (CSNH<sub>2</sub>). <sup>13</sup>C NMR spectrum ( $\delta$ , ppm): 15.3 q (J = 140 Hz, SMe), 140.6 (C<sup>4</sup>), 145.9 (C<sup>5</sup>), 186.9 (C=S). Found: C, 27.6; H, 3.4; N, 32.2; S, 36.8%. Calculated for C<sub>4</sub>H<sub>6</sub>N<sub>5</sub>S<sub>2</sub>: C, 27.9; H, 3.7; N, 32.2; S, 36.9%.

5-Methylthio-1-methyl-1,2,3-triazole-4-carbothioamide (Vb) was obtained by analogy to (Va) from thiadiazole (IIb) [2] (method A) or from triazole (VIb) [2] (method B). The physicochemical indices of the two samples coincided, mp 112°C. UV spectrum ( $\lambda_{max}$  (log  $\varepsilon$ ), nm): 243 (2.95), 296 (2.88). PMR spectrum ( $\delta$ , ppm): 2.5 s (SMe), 4.1 s (Me), 9.4 s (CSNH<sub>2</sub>). <sup>13</sup>C NMR spectrum ( $\delta$ , ppm): 18.0 q (J = 143 Hz, Me), 35.5 q (J = 143 Hz, SMe), 133.5 (C<sup>4</sup>), 146.8 (C<sup>5</sup>), 188.2 (C=S). Mass spectrum, m/z (relative intensity, %): M<sup>+</sup> 188 (100), 173 (80), 81 (95), 72 (89), 60 (66). Found: C, 32.2; H, 4.4; N, 30.0; S, 34.1%. Calculated for C<sub>5</sub>H<sub>8</sub>N<sub>4</sub>S<sub>2</sub>: C, 31.9; H, 4.3; N, 29.8; S, 34.0%.

 $\begin{array}{l} \textbf{5-(3-Phenylureido)-1,2,3-thiadiazole-4-S-methylthioimidate (III) was obtained by analogy to (Va) from thiadiazole (I) according to method A in 71% yield, mp 185°C. IR spectrum (<math>\nu$ , cm<sup>-1</sup>): 3250, 3140 (NH), 2960 (CH), 1685 (C=O). PMR spectrum ( $\delta$ , ppm): 2.7 s (SMe), 7.0-7.7 m (Ph, NH), 10.1 s (NH), 12.0 s (NH). ^{13}C NMR spectrum ( $\delta$ , ppm): 12.4 q (J = 142 Hz, Me), 137.7 (C<sup>4</sup>), 157.3 (C=NH), 161.4 (C<sup>5</sup>), 170.8 (C=O). Found: C, 45.4; H, 4.1; N, 24.3; S, 21.9%. Calculated for  $C_{11}H_{11}N_5OS_2$ : C, 45.1; H, 3.8; N, 23.9; S, 21.8%.

## LITERATURE CITED

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